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The role of inorganic and organic nutrients on the development of phytoplankton along a transect from the Daugava River mouth to the Open Baltic, in spring and summer 1999

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The importance of dissolved silicate (DSi), dissolved inorganic nitrogen (DIN), dissolved organic nitrogen (DON), phosphate and dissolved organic phosphorus (DOP) on algal growth is analysed for the Gulf of Riga and the adjacent open Baltic Sea. The results of three cruises (May, June, and July, 1999) along a transect across the Gulf of Riga from the entrance to the Daugava River to the open Baltic are presented. Nutrient-limitation was identified on the basis of available nutrient concentrations and stoichiometric analysis. In spring, phosphate appeared to be the algal-growth-potential-limiting nutrient at the entrance of the Daugava River, DSi in the central Gulf, and DIN at the open Baltic station. There was no correlation between limiting nutrient and spring phytoplankton community structure. Both the DIN and phosphate pools of the upper mixed layer were exhausted by mid-May, except at the river mouth. In summer there was a good correlation between phytoplankton biomass and DOP along the transect. Contrary to the situation in the open Baltic, the lower layer DIN/phosphate ratio in the Gulf of Riga significantly exceeds the Redfield ratio, and upwelling likely does not favour nitrogen-fixing species. Therefore, the upper layer DOP pool should be regarded as potentially the main source of phosphorus for nitrogen-fixing cyanobacteria in the Gulf of Riga.

Keywords: Baltic Sea, community structure, DON, DOP, Gulf of Riga, inorganic nutrients, phytoplankton.

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Introduction

Anthropogenic activity has resulted in increased and unbalanced algal nutrients input to estuarine and coastal waters, which in turn has affected the comparative levels of available nutrients in the adjacent sea. It is widely accepted that such changes can impact phytoplankton community development in terms of both biomass and dominant taxa (Cederwall and Elmgren, 1990; Kahru *et al.*, 1994; Escaravage *et al.*, 1996; Schöllhorn and Granéli, 1996). This process is evolving faster in areas such as the semi-closed Gulf of Riga (eastern Baltic Sea), which falls under the influence of discharges from the Daugava River. Knowledge of the relationship between nutrients and phytoplankton in such areas could be of value to those charged with advising environmental decision-makers.

Long-term trends in inorganic nutrient concentrations in the Gulf of Riga have been documented by Yurkovskis *et al.* (1993), who concluded that the Gulf was phosphorus-limited, in contrast to the open waters of the Baltic, which are regarded as nitrogen-limited (Granéli *et al.*, 1990; Kivi *et al.*, 1993). The conclusions of those authors were based on the ratio between dissolved inorganic nitrogen (DIN) and phosphate, and therefore Põder and Jaanus (1997) anticipated a changed DIN/phosphate ratio in the Irbe Strait, which separates the Gulf of Riga from the open Baltic. However, their study in the summers of 1993 and 1994 did not show the expected change in ratio, so contradicting the thesis of a limiting nutrient dichotomy in the Gulf of Riga and the open Baltic. Subsequently, it has been suggested that the Gulf of Riga is basically nitrogen-limited, with phosphorus being limiting only where the Gulf is influenced by discharge from the Daugava River (Maestrini *et al.*, 1999a; Tamminen and Seppälä, 1999). However, none of the studies listed considered possible seasonal differences in algal-growth-potential (AGP)-limitation, or dissolved organic matter (DOM) as a potential source of nutrients. At the same time, the results of experiments carried out with natural populations of phytoplankton from the Gulf of Riga and a few cultured algal strains suggested that cyanobacteria could sustain growth by an uptake of dissolved organic nitrogen (DON) of terrestrial origin (Balode *et al.*, 1998; Maestrini *et al.*, 1999b). Further, Nausch (1998) presented evidence that, at low concentration of phosphate, some dissolved organic phosphorus (DOP) compounds could be used by Baltic phytoplankton. The potential role of dissolved silicate (DSi) had also been overlooked despite Pitkänen and Tamminen (1995) already detecting silicate-limitation in another region of the Baltic.

The aim of this article is to investigate the role of nutrients, including DSi, DON, and DOP, on the development of phytoplankton communities in the Gulf of Riga during spring and summer.

Material and methods

Sampling took place at five stations along a transect from the mouth of the Daugava River out into the open Baltic Sea (Figure 1) in 1999, at the expected periods of spring bloom (5–10 May), post-bloom (6–11 June) and midsummer (26–30 July) stages. Stations 101 and 119 were in the area of the Daugava River plume, station 121 in the central Gulf of Riga, station 114 in the Irbe Strait, and station 34a in the adjacent open Baltic.

Sampling was always between 08:30 and 09:00 local time, in order to sample phytoplankton at the same phase of its diel physiological cycle and possible vertical migration. A vertical profile of salinity and temperature was first taken to determine the depth of the pycnocline separating the upper mixed layer from the deeper layer. Water samples were taken with 10-l Niskin bottles at five depths in each layer (2–3 depths in shallow water), and pooled into two 50-l integrated samples, representing the average hydrochemical and phytoplankton conditions of those layers.

Subsamples for dissolved organic nutrients determination were filtered on board onto combusted (450°C) and HCl-rinsed Whatman GF/F filters. The samples were then frozen and taken ashore to the laboratory at Pärnu for analysis of nutrient content. Inorganic nutrients (nitrate, ammonia, phosphate) were measured with a Skalar autoanalyser system using standard analytical protocols ISO 6878, 1996; ISO 11732, 1997; ISO 13395, 1999). Silicate was measured according to Koroleff and Grasshoff (1983). DIN in this context represents the sum of nitrate (+nitrite) and ammonia. Total nitrogen and phosphorus were obtained following the persulphate digestion procedure of Koroleff and Grasshoff (1983), and then treated as for soluble reactive nitrogen and phosphorus. DON was calculated as the difference between total nitrogen in the filtrate and DIN concentrations, and DOP as total phosphorus minus orthophosphate concentration. Urea was analysed manually according to the method described by Koroleff and Grasshoff (1983). Dissolved free amino acids (DFAA) were measured according to the protocols of Möpper and Lindroth (1982) and Petty *et al.* (1982). Phytoplankton samples were preserved with acid Lugol's solution and analysed according to Utermöhl (1958). Phytoplankton biomass was calculated in terms of a biovolume, according to standard Baltic protocol (Edler, 1979).

Results

May

Water temperature was highest (9.0°C) near the mouth of the Daugava River (at station 101) and lowest (4.1°C) in the Irbe Strait (station 114), where there was an inverted temperature stratification. The upper mixed layer salinity increased from 0.8 PSU at station 101 to 4.3 PSU in the central Gulf (station 121), to 6.6 PSU in the open Baltic (station 34a). There was a well-defined vertical density structure at all stations. The depth of the pycnocline varied from 6 m at station 119 to 20 m in the central Gulf.

Nutrient concentrations nearshore were high, indicating that discharge from the Daugava River was influencing nutrient conditions. At both nearshore stations (stations 101 and 119) silicate concentration decreased with depth, from some 25 µM in the upper layer to 6–9 µM in the lower layer. In the central Gulf the whole water column was depleted of silicate, concentrations being <0.6 µM in both upper and lower layers. The Irbe Strait upper mixed layer was also somewhat silicate-depleted, but the DSi concentration increased below the pycnocline. In contrast to other inorganic nutrients, the upper layer silicate pool was not exhausted in the open Baltic (Figure 2). DIN concentration decreased by an order of magnitude between the area adjacent to the river discharge and the central Gulf (Figure 3). In the Irbe Strait and the open Baltic, the whole water column was DIN-depleted. Nitrate and ammonia contributed differently to the overall DIN concentration. Nitrate was the dominating fraction nearshore whereas ammonia dominated in the Irbe Strait and the open Baltic. DON

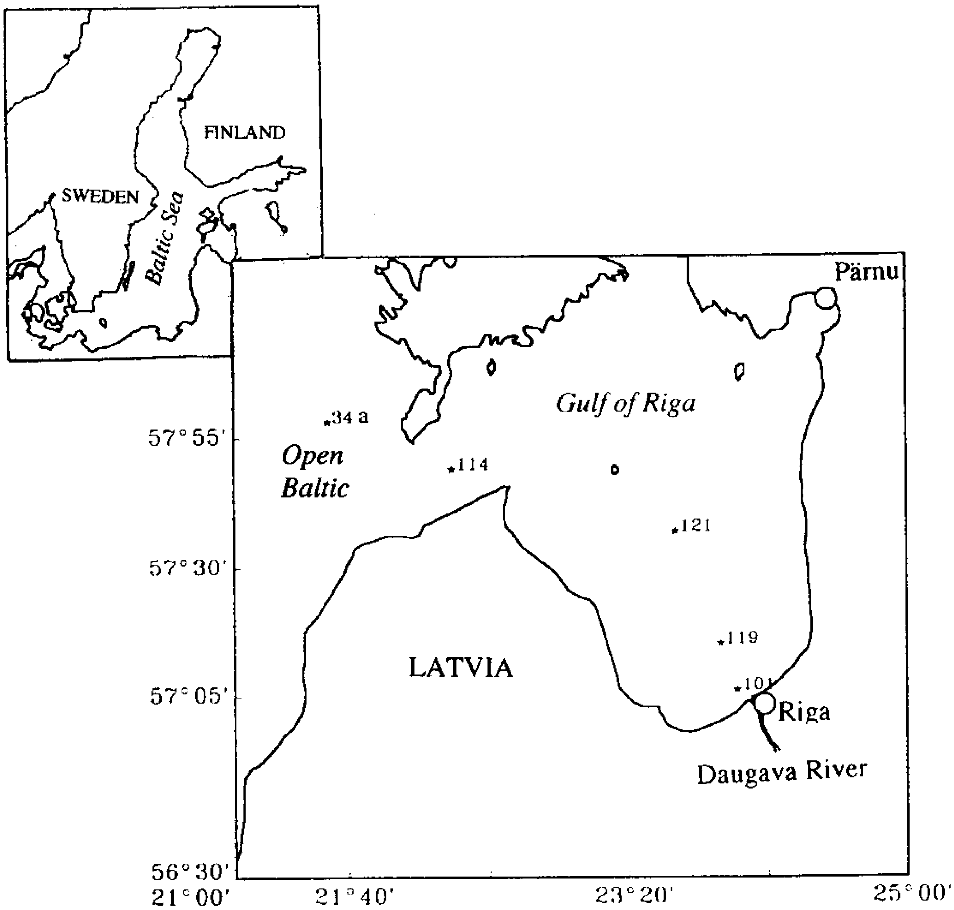

Figure 1. Location of sampling stations along the transect from the Daugava River mouth to the open Baltic.

concentration decreased more than twofold along the transect (Figure 3). Two fractions of DON, urea and DFAA, were analysed separately. The concentration of urea was fairly uniform over the whole transect, mostly around 3–4 μM, although concentrations were slightly higher in the Daugava River plume. DFAA concentrations fluctuated within the range 0.1–0.4 μM, without any clear spatial trends. The dynamics of phosphate concentration followed principally those of DIN, but with smaller gradients (Figure 4). As for DON, both horizontal and vertical variabilities in DOP concentration were limited, being mainly in the range 0.3–0.7 μM.

Phytoplankton biomass was highest in the central Gulf and Irbe Strait, and less than half those values in the open Baltic and nearshore (Figure 5). Diatoms (Bacillariophyceae) dominated all Gulf stations, constituting on average 70% of total phytoplankton biomass, the percentage peaking (82%) near the entrance to the river. Dinoflagellates (Dinophyceae) were the second most widespread group, increasing proportionally along the transect from nearshore to offshore. They dominated biomass in the open Baltic.

June

The horizontal structure of the temperature field in the upper layer at the beginning of June was indicative of speedier warming in the Gulf than in the Irbe Strait and the open Baltic. In the upper layer too, salinity increased gradually along the transect from the Daugava plume to the open Baltic. Moreover, salinity in the Gulf had increased since May, indicating probably a reduction in the discharge level of the Daugava River. The vertical distribution of temperature and salinity above the pycnocline was uniform, except at the Daugava River station, where both temperature and salinity increased smoothly without any pycnocline-forming gradients, and the mixed layer reached the bottom. At some stations, the upper mixed layer reached a depth of 15 m.

The strong gradients in upper mixed layer DIN observed in May had disappeared, likely because of the decline in river discharge. Compared with May, the main Gulf area had become even more silicate-depleted, the upper mixed layer concentrations being <0.3 μM. DSi increased in the Irbe Strait and was even higher in the open Baltic (Figure 2).

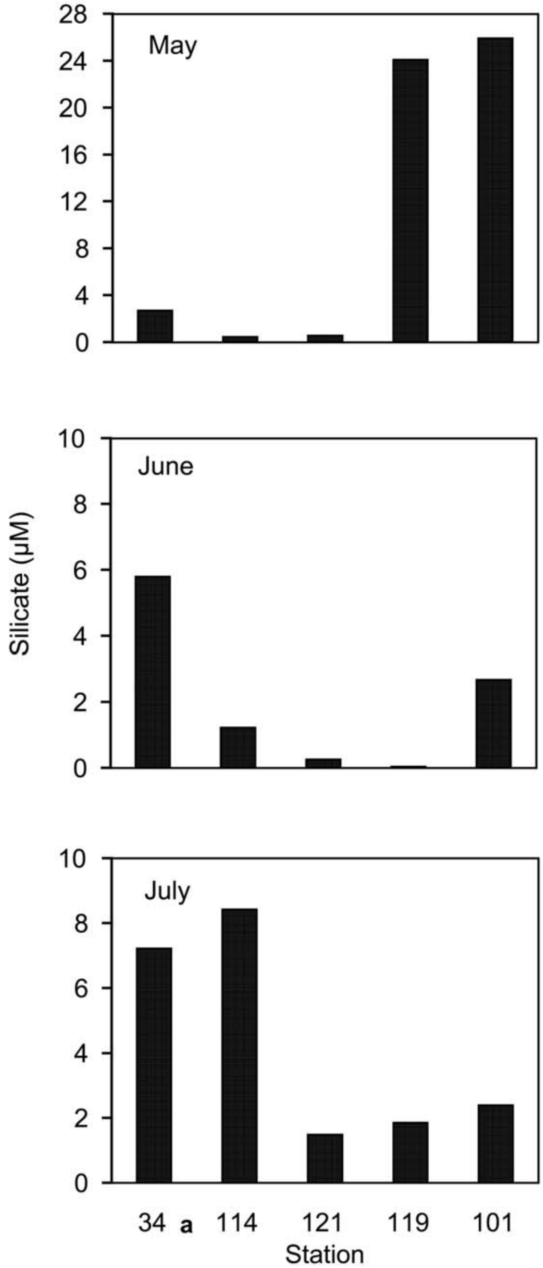

Figure 2. Silicate concentrations in the upper mixed layer of the Gulf of Riga and adjacent Baltic Sea, May–July 1999.

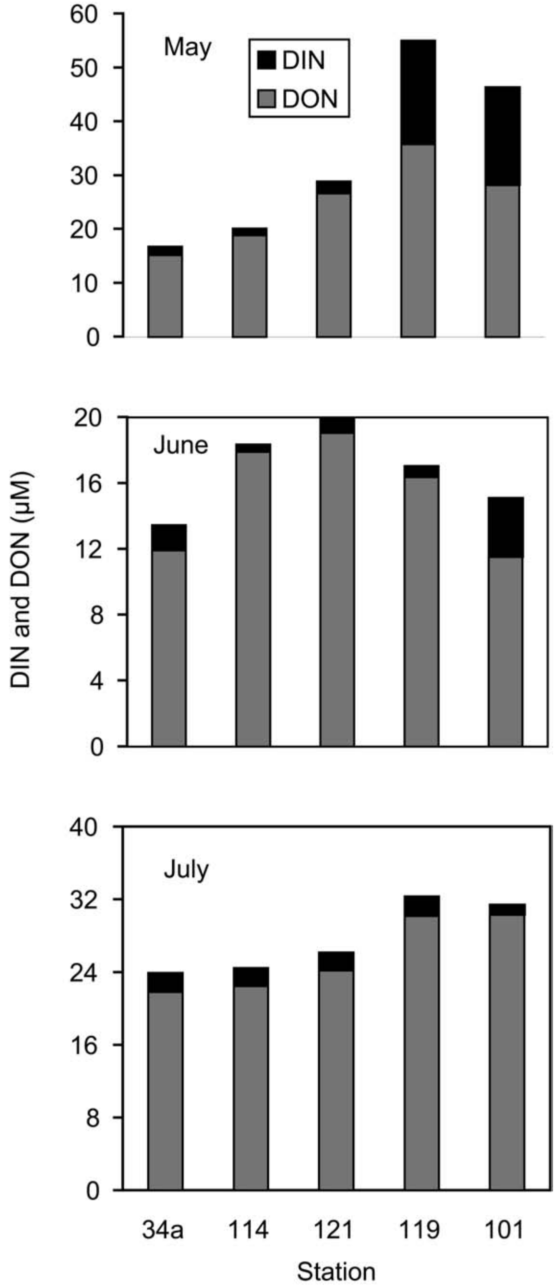

Figure 3. DIN and DON concentrations in the upper mixed layer of the Gulf of Riga and adjacent Baltic Sea, May–July 1999.

Other than at the Daugava River mouth, the upper mixed layer across the whole transect had become DIN-depleted (<1 µM); at the river mouth concentrations remained at 3–4 µM (Figure 3). Ammonia dominated the upper mixed layer DIN pool, except in the Daugava plume, where nitrate dominated. Both horizontal and vertical concentration gradients of DON were weak, values ranging mainly between 10 and 20 µM. DON concentrations in the upper mixed layer had approximately halved nearshore since May (Figure 3). The same trend of decreased concentration nearshore was observed for urea, but DFAA concentration had remained the same as in May. The upper mixed layer phosphate pool was exhausted over most of the transect and exceeded 0.1 µM only at the entrance to the Daugava River. The upper layer DOP concentration had not changed much since May (Figure 4). At all stations except

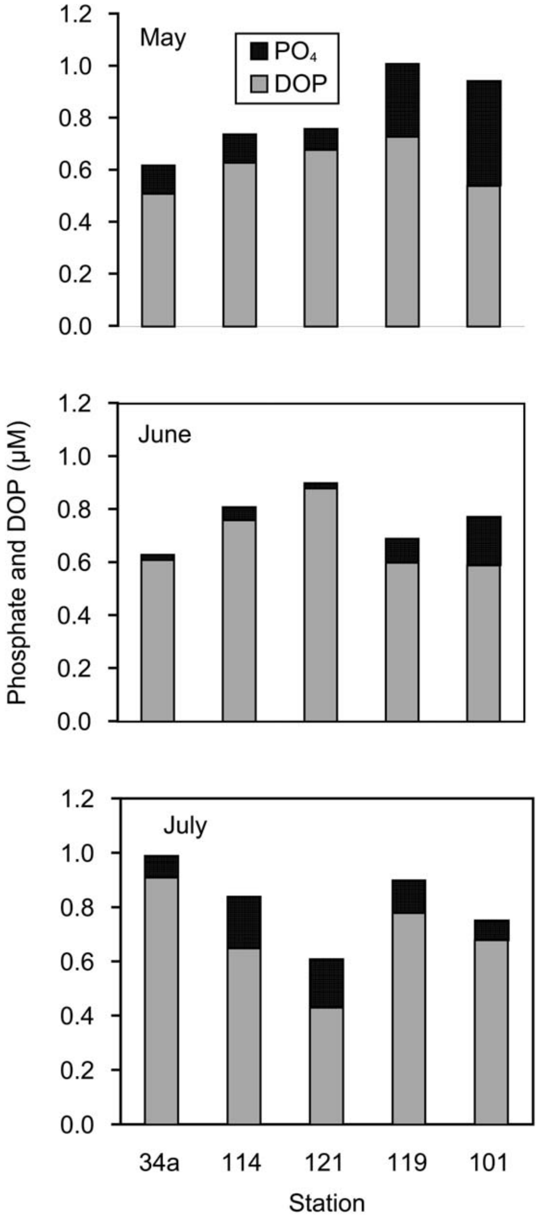

Figure 4. Phosphate and DOP concentrations in the upper mixed layer of the Gulf of Riga and adjacent Baltic Sea, May–July 1999.

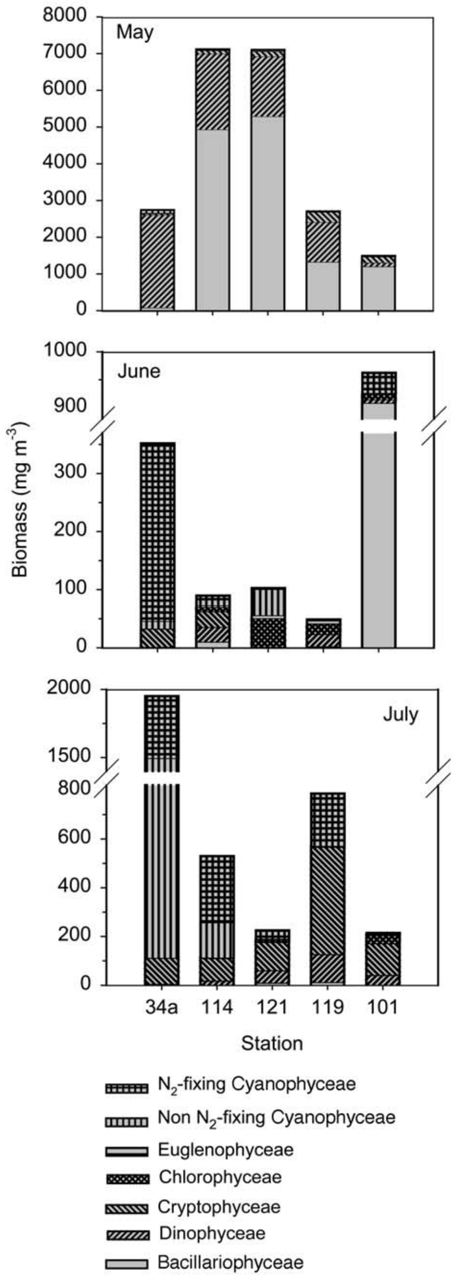

Figure 5. Phytoplankton biomass and community structure in the Gulf of Riga and adjacent Baltic Sea, May–July 1999.

in the Daugava plume, DOP concentrations below the pycnocline slightly exceeded those in the upper mixed layer.

Compared with May, phytoplankton biomass was greatly reduced, at all stations (Figure 5). The highest biomass, dominated (95%) by the diatom *Skeletonema costatum*, was at the Daugava River entrance. At other Gulf stations and in the Irbe Strait, total phytoplankton biomass was an order of magnitude lower ($\leq 100\,mg\,m^{-3}$). In most of the Gulf and in the Irbe Strait, cyanobacteria (Cyanophyceae) and dinoflagellates dominated the phytoplankton, but there was no clear spatial trend. The second largest phytoplankton biomass was in the open Baltic, where nitrogen-fixing cyanobacteria dominated to the tune of 87% of biomass.

July

Surface temperature in June was uniformly high (19.3–20.2°C) along the whole transect, except in the Irbe Strait, where it was just 17.3°C, indicating recent upwelling. The depth of the pycnocline had shifted to 12–16 m in the Gulf and to 20 m in the open Baltic.

Concentrations of inorganic nutrients were slightly higher in the upper mixed layer than in June. The distribution of silicate along the transect was basically the same as the previous month (Figure 2), although the upper mixed layer DSi concentration had increased at all stations except in the Daugava plume. By the end of July, DIN concentration had dropped at the river entrance and increased slightly at the other stations. This had resulted in homogeneously low DIN concentrations across the whole transect above the pycnocline (Figure 3). At all Gulf stations the lower layer DIN concentration exceeded 10 μM, but it remained <3 μM in the open Baltic. As in June, the DON concentration was uniform along the transect, but slightly higher nearshore. The concentration of urea had decreased slightly to the range 1.5–2.5 μM, without any evident spatial pattern. The variability of DFAA concentration had also decreased, most values being within the range 0.1–0.2 μM. Phosphate concentrations were similar to those of DIN: a small decrease in the upper mixed layer at the Daugava mouth and a slight increase at other stations (Figure 4). Beneath the pycnocline, phosphate concentration had increased further, to 0.45 μM at stations 119 and 121. In general, the lower layer phosphate concentration within the Gulf was double the corresponding value in the open Baltic. DOP concentration varied between 0.3 and 0.9 μM in all samples, and vertical gradients were noticeable only nearshore, where DOP dropped to about 0.2 μM below the pycnocline.

Compared with June, phytoplankton biomass had increased along the transect, except at the Daugava River mouth, where diatoms had disappeared and increases in the biomass of other taxa could not compensate for their disappearance (Figure 5). In contrast to June, highest phytoplankton biomass was not actually in the Daugava plume, but at the next station seawards (station 119), where it was three times higher than at other stations. Cryptophytes dominated all stations. Phytoplankton biomass was greater in the Irbe Strait and greater again in the open Baltic, at which station cyanobacteria dominated.

Discussion

Phytoplankton biomass nearshore was too small in May 1999 (spring) to be regarded as a bloom peak; Seppälä and Balode (1999) reported a phytoplankton biomass about an order of magnitude higher at the Daugava River mouth in April 1995. On that basis, the bloom was either still building up or had started to decay. The relatively high inorganic nutrient concentrations support the first option. Development of the bloom at the river entrance could also be impacted by freshwater discharge and dilution (Yin *et al.*, 2000). However, owing to the inflow of fresh inorganic nutrients, the decline of the bloom seems to have progressed rather slowly. At station 101 close inshore, phytoplankton biomass and nutrient concentrations were still high in June. Also, despite the rather high water temperature (about 14°C), diatoms continued to dominate. Only by July had both DIN and phosphate concentrations declined at the river entrance, while silicate concentration still persisted at about 2 μM. Thus, either DIN or phosphate is limiting the spring AGP at the Daugava River mouth. The DIN/phosphate ratio of 45 at station 101 in May significantly exceeded the Redfield ratio (16), and could perhaps therefore be interpreted as evidence of phosphate-limitation. Possible phosphate-limitation nearshore in the Gulf of Riga has been documented before (Tamminen and Seppälä, 1999). However, other factors, such as light-limitation caused by self-shading or an increase in the depth of mixing, have been advanced as explanations of spring bloom decline in coastal areas (Olli and Heiskanen, 1999), and evidences of metal-limitation in estuarine waters have also been reported (Zhang, 2000). It is therefore likely that phytoplankton development in a highly dynamic plume area is controlled by multiple interacting factors, changing in time and space. The dynamics of the spring bloom at the next station seawards (station 119) are different. In May the station was seemingly influenced by the Daugava River discharge, with its high concentration of inorganic nutrients. Later, owing to the decline of riverine outflow, station 119 was beyond the edge of the Daugava plume, and the dynamics of the phytoplankton community were analogous to those of the central Gulf and the Irbe Strait.

A high biomass of diatoms and low concentrations of inorganic nutrients above the pycnocline are a clear sign that a bloom is either close to its peak or perhaps already starting to decline. That was the situation in the central Gulf and Irbe Strait in early May. Phytoplankton biomass values were similar to values given in the literature for blooms in the Gulf (Seppälä and Balode, 1999). The extremely low concentration of silicate (about 0.5 μM) at stations 121 and 114 in May and even less at station 119 in June indicate that silicate could be the spring diatom-bloom-limiting nutrient in most of the Gulf of Riga. Nelson and Dortch (1996) stated that the growth rate of most diatoms is likely limited at a silica concentration of 0.5 μM, and based on the results of an enclosure experiment, Carlsson and Granéli (1999) suggested that diatoms are probably unable to decrease a silica concentration below 0.55 μM. A hypothesis of silicate-limitation in this case is supported by examining inorganic nutrient ratios in the phytoplankton and in ambient water. Averaged molar ratios of nutrients in cell contents, $C/Si = 7.69$ (Brzezinski, 1985), $C/N = 6.62$ and $C/P = 106$ (Redfield, 1934), result in $N/Si = 1.2$ and $Si/P = 14$. At station 121 in this study, the DIN/DSi ratio was 4 and the DSi/phosphate ratio was 7, clearly indicative of AGP silicate-limitation. Earlier studies on spring bloom nutrient-limitation in the Gulf of Riga have focused on two alternatives—DIN and phosphate. Tamminen and Seppälä (1999) pointed out that the spring phytoplankton bloom in the Gulf is overwhelmingly nitrogen-limited, but that phosphate-limitation would likely take place nearshore. The same authors did not consider silicate as a potential alternative limiting factor. Suursaar (1995) and Olli and Heiskanen (1999) felt that silicate would be unlikely to limit the growth of diatoms in the Gulf of Riga, but the current results seem to disprove that thesis and lend support to Yurkovskis (1998) and Yurkovskis *et al.* (1999), who state that silicate can be limiting.

A low phytoplankton biomass coupled with extremely low DIN and phosphate concentrations indicates that the spring bloom was already declining in the open Baltic by 10 May. A silicate concentration >2 μM at the end of bloom implies that, in contrast to waters of the Gulf of Riga, silicate was not the AGP-limiting nutrient. The DIN/phosphate ratio of 14 at the open Baltic station is slightly below the Redfield ratio and indicative of DIN-limitation. However, the Redfield ratio is an average value, and a low phosphate concentration significantly decreases the precision of calculation of the ratio. Nevertheless, even if not that convincing on their own, our results do not contradict the idea that nitrogen can be limiting in the open Baltic (Granéli *et al.*, 1990; Kivi *et al.*, 1993).

Our results do show that DOP concentration in the phosphate-exhausted Daugava plume as well as DON concentration in the DIN-exhausted open Baltic did not change much between May and June. Therefore, we believe that DOP and DON concentrations had little influence on spring diatom bloom development.

We expected silicate-limitation to have further implication in the determination of dominant species during a spring bloom. However, our data do not reflect any correlation between silicate-limitation and dinoflagellate abundance. The biomass of dinoflagellates increased along the transect and seemingly correlated with the timing of the bloom. A shift from diatom to dinoflagellate dominance during a spring bloom has been recorded before (Tamminen, 1995; Seppälä *et al.*, 1999) and seems to be common. Heterotrophic dinoflagellates can be major grazers on a spring bloom, ingesting large diatoms (Tiselius and Kuylenstierna, 1996).

One could expect silicate- and nitrogen-limitation to have resulted in unused phosphate remaining in the upper mixed layer after the decay of the spring bloom. In this case, the upper mixed layer phosphate pool was completely exhausted by early June, so perhaps the phosphate left by silicate-limited diatoms was utilized by dinoflagellates or other non-silicate-dependent species at the final stage of the bloom.

Several studies (e.g. Tamminen and Seppälä, 1999) have demonstrated that the summer (in this case, June and July) upper mixed layer DIN/phosphate molar ratio is low (less then 16) in the Gulf of Riga, and regard this as proof of nitrogen-limitation. Moreover, summer nitrogen-limitation has been advanced as an explanation of increased abundance of nitrogen-fixing cyanobacteria, sometimes causing harmful blooms (Cederwall and Elmgren, 1990; Kahru *et al.*, 1994; Escaravage *et al.*, 1996; Schöllhorn and Granéli, 1996). Despite the seemingly favourable ambient conditions of warm temperature and calm weather and an upper mixed layer DIN/phosphate ratio of around 10, the biomass of nitrogen-fixing cyanobacteria in the Gulf and open Baltic stations was low in July 1999. This suggests once again that suggesting a deterministic causal link between the DIN/phosphate ratio and cyanobacteria growth is too simplistic.

Unreliability related to a large relative analytical error (summer nutrient analysis close to the detection limit) has been mentioned earlier (Maestrini *et al.*, 1999a, b). Moreover, the implication of an available N/P ratio itself will change when the apparent nutrient concentrations are low: the ratio has no relevance to the discussion when the pools of both nutrients are close to zero, as often happens in the upper mixed layer of the Baltic Sea in summer. Convincing objections to a deterministic interpretation of the N/P ratio are presented by Reynolds (1999). Finally, the role of DON and DOP as nutrient sources could significantly increase when there is insufficient DIN and phosphate available. There is convincing information that urea and DFAA can be used by phytoplankton (Pettersson and Sahlsten, 1990; Antia *et al.*, 1991; Tamminen and Irmisch, 1996; Berg *et al.*, 2001). Replacing DIN with available nitrogen (DIN+urea+DFAA), the nitrogen/phosphate molar ratio will elevate the ratio above 16 (ranging between 21 and 51) at all stations. However, it is questionable whether urea and DFAA ought to be regarded as nitrogen sources for use by phytoplankton under all conditions. In contrast to DIN, no vertical gradient of urea concentration was detected in this study, and the same observation was made in the Skagerrak by Pettersson and Sahlsten (1990). On the other hand, some fractions of DOP could also be used by phytoplankton (Nausch, 1998). Unfortunately, the proportion of the DOP pool available to cyanobacteria is not yet known. Therefore, a DIN/phosphate ratio cannot provide an adequate indication of summer AGP-limitation in the Gulf of Riga and should be replaced by an available N/P ratio. However, the latter assumes much better quantification of available organic nutrient fractions than is possible now.

Another approach to obtaining information about the interactions between phytoplankton and dissolved organic nutrients is to examine their spatial distribution. Comparison of algal biomass and DOP distribution along the transect in July reveals clear coincidence between biomass and DOP changes, whereas the spatial distribution of DON was rather uniform. Nevertheless, it is impossible to attribute causal links to the correlation between DOP and phytoplankton biomass, because the increased nitrogen-fixing cyanobacteria biomass in the Irbe Strait upwelling area may have been relying on a fresh supply of phosphate from relatively phosphorus-rich and DIN-poor (DIN : phosphate$\sim$3) deep water seawards of the Irbe Strait. Wind-induced vertical-mixing-related nutrient pulses have promoted cyanobacterial blooms in other parts of the Baltic Sea (Kononen *et al.*, 1996).

In any event, the residual phosphate <0.05 μM at the end of a spring bloom could support only negligible AGP in summer. Therefore, the bloom of nitrogen-fixing cyanobacteria would not be possible without additional phosphorus. Potential alternative sources are the transport of phosphate from the lower layer by upwelling, and DOP in the upper mixed layer (direct uptake and/or regeneration via microbial loop). In contrast to the open Baltic, the lower layer water of the Gulf of Riga is DIN-rich, resulting in a high DIN/phosphate ratio (about 28 in July). Therefore, the upwelled lower layer water in the Gulf would not provide advantage for nitrogen-fixing cyanobacteria, so it is likely that blooms of nitrogen-fixing cyanobacteria in the Gulf of Riga are primarily dependent on the DOP.

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